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Phosphorescence decay of holmium activated strontium sulphide phosphors

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Sixteen samples of SrS : Ho phosphors have been prepared. The concentration of holmium was varied by weight in successive steps. Phosphorescence decay has been observed at room temperature by exciting the phosphors with UV lamp (3650 Å) and the intensity has been measured with the help of photomultiplier tube IP 21. It is concluded that the decay is of the form $I_t = I_0 t^{-b}$ where the values of b vary from 0.69 to 0.88. By peeling off the curves into three exponentials, it is estimated that at room temperature (28°C) traps having depth of 0.623 ± 0.057 eV are effective, justifying the applicability of Ramdall & Wilkins (1945) theory which neglects retrapping. The results are satisfactorily explained on the basis of superposition theory, assuming the kinetics to be monomolecular.

1. Introduction

Alkaline earth sulphide phosphors are one of the earliest known phosphorescent materials. Interest in this class of phosphors has been rejuvenated with the discovery of infrared stimulation and sensitised luminescence. The decay characteristics offer significant information about the kinetics involved in the luminescence process and the energy distribution of trapping centres. In the present investigation holmium activated SrS phosphors have been successfully prepared and their decay studied.

2. Phosphors Preparation and Experimental Procedure

A series of phosphors SrS : Ho (0.0001 to 0.11 gm.) containing sixteen samples was prepared, these were synthesised with 20% flux (sodium thiosulphate) in 10 gms of $SrSO_4$ at 930 ± 10°C. The reducing agent was A.R. grade carbon powder. The phosphors were excited by ultraviolet light (3650 Å). The after glow intensity was measured with a photomultiplier IP21 and multiflex galvanometer from 5 sec after the cessation of excitation to a time when it decayed to a negligibly small value.

3. Results

The theory of Randall & Wilkins (1945a) for emptying of traps assumes that the probability p of an electron escaping from a trap is given by

$$p = S \exp(-E/kT). \qquad \ldots (1)$$

The above equation assumes that the electron freed from traps are not retrapped that S and E are independent of temperature and that the freed electrons undergo radiative rather than non-radiative transitions. Then for a single trap level, the intensity decays as

$$I_t = I_0 \exp(-pt), \qquad \ldots (2)$$

where $I_0 = n_0 p$, n_0 being the number of electrons in traps of depth, E at time $t = 0$. This gives an exponential decay. If, however, there is a distribution of trapping levels, the observed phosphorescence is due to a superposition of intensities, each intensity varying exponentially with time. The form of the decay curve obtained by plotting the logarithm of intensity as a function of time is then hyperbolic (figure 1).

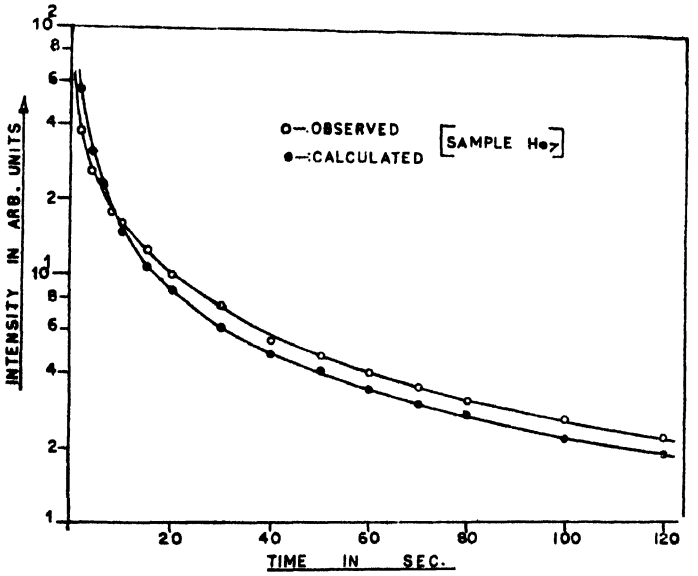

Fig 1. Observed and calculated decay curves for the sample Ho_7.

Analysis of Decay Curve : Following Bube (1950) and others (Curie 1963) the decay curves were analysed into three exponentials by the method of successive subtraction (figure 2). The trap depth corresponding to each exponential was evaluated by using eq. (1) and assuming $S = 10^9$/sec at room temperature (301°K) (Sinha & Sivaraman 1972).

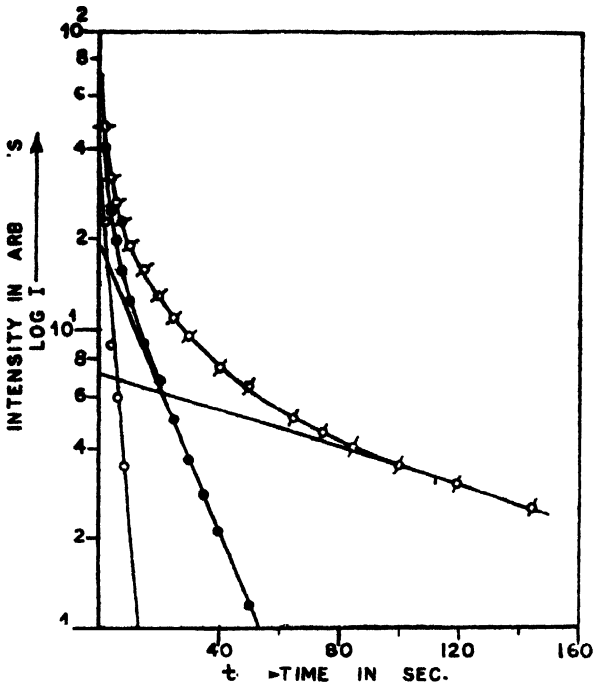

Fig. 2. Peeling off the decay curve.

4. Discussion

In the present studies the observed decay curves are hyperbolic in nature. On the basis of superposition theory the observed phosphorescence intensity will be due to all the exponentials. If n represents the number of electrons, then for the uniform distribution of the trapping levels, the following relation holds good (Randall & Wilkins 1945b)

$$I_t = \frac{nST}{t}(1 - e^{-tS})$$

In the present case, $St >> 1$. Therefore the equation reduces to

$$I_t = nSTt^{-1}.$$

However, the observed decay is of the form

$$I_t = I_0 t^{-b},$$

where b varies from 0.69 to 0.88. This deviation of decay constant from unity excludes the possibility of uniform distribution of trapping states. The comparatively small variation of decay constant with activator concentration suggests that the activator only modifies the relative importance of the trap but not their mean depth. Hence the distribution of traps can be assumed to be quasi-uniform.

There is no regular pattern in which the decay constant may vary. The variation in the decay constant may be due to the relative variation in the trap distribution. The variation in the activator concentration also affects the number of non-radiative transition due to concentration quenching which are also likely to affect the value of decay constant. The absorption in the material has not been taken into account and it is likely to vary due to the presence of unreacted materials which are very difficult to remove. Hence the variation in decay constant with activator concentration may be a much more complicated effect. The deviation may be due to this uncertainity in the composition of the phosphors. Further it is also not possible to keep the size of the grain the same, which also affects the results as observed by various workers.

The traps which contribute significantly to the phosphorescence intensity under the present study have depth in the region of 0.566 to 0.681 eV. This is identical with the values of trap depths determined by earlier workers (Sivaraman & Bhawalkar 1971, Jain & Ranade 1973), irrespective of flux or activator used, under the identical experimental conditions (Agnihotri & Ranade 1968, Sharma & Singh 1969). Curie (1963) observed that the trap group corresponding to about 0.68 eV is independent of activator concentration. So it appears that this particular group of traps is characteristic of the host lattice itself.

References

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